cium almost impossible. This separation, however, is readily effected by bisulphite of soda.

III. *Action of Sodium and Amyl Iodide upon Acetic Ether.*

For this reaction the compounds of sodium derived from acetic ether were prepared as before, and were then submitted to the action of amylic iodide for several hours at the boiling-point of the mixture. When the sodium had all become converted into iodide, water was added and the supernatant liquid decanted. We reserve a complete description of this liquid for our next communication, and will here confine ourselves to the separation from it of œnanthylic acid, which was obtained as follows:—The crude product, after drying over chloride of calcium, was submitted to rectification, and the portion boiling between 170° and 190° C. collected apart and decomposed by ebullition with alcoholic potash. By this treatment we destroyed any ethylic amylacetone carbonate and ethylic diamylacetone carbonate that were present, and obtained a potash-salt of an acid derived from acetic acid by the substitution of one atom of amyl for one of hydrogen. The potash-salt thus obtained was distilled with excess of sulphuric acid diluted with a large quantity of water. Upon the distillate there floated an oily acid, possessing an odour resembling œnanthylic acid. This acid was converted into an ammonia-salt, from which a silver-salt was prepared by precipitation. After being well washed with cold water, this salt yielded numbers on analysis closely corresponding with the formula of amylacetate or œnanthylate of silver:

$$C_2\left\{\begin{array}{l} C_5\,H_{11} \\ \underline{H_2} \\ O'' \\ O\,Ag \end{array}\right.$$

We have also examined the barium-salt, which is an amorphous soapy substance. Dried at 100° C., ·2715 grm. gave ·1599 grm. of barium sulphate, corresponding to 34·62 per cent. of barium. Barium œnanthylate contains 34·69 per cent. of barium. We believe amylacetic acid to be identical with œnanthylic acid.

The concluding portion of the paper is devoted to a discussion of the theoretical bearings of the reactions above described, and to the investigation of the internal architecture of the synthetically prepared ethers, acids, and ketones.

II. "Researches on the Hydrocarbons of the Series $C_n\,H_{2n+2}$."—No. II. By C. Schorlemmer, Esq., Assistant in the Laboratory of Owens College, Manchester. Communicated by Prof. H. E. Roscoe. Received July 20, 1865.

From my experiments communicated to the Royal Society on the 6th of April, 1865, I concluded that the question, whether only one series of hydrocarbons of the general formula $C_n\,H_{2n+2}$ exists, or whether this

series exhibits cases of absolute isomerism, can only be definitely decided by obtaining from different sources perfectly pure hydrocarbons, having the same composition. But unfortunately only a few of the hydrocarbons can be obtained perfectly pure, and still fewer of these possessing the same composition can be derived from different sources. This is seen by a glance at the following Table, containing those alcohol-radicals and hydrides which have been obtained with certainty in a pure state.

		Boiling-points.		Boiling-points.
$C_2 H_6$	Methyl.		Hydride of ethyl.	
$C_4 H_{10}$	Ethyl.		——	°
$C_5 H_{12}$	——	°	Hydride of Amyl	30
$C_6 H_{14}$	Ethyl-butyl	62	Hydride of hexyl * ..	69·5
$C_7 H_{16}$	Ethyl-amyl..........	90	Hydride of heptyl † ..	99
$C_8 H_{18}$	Butyl..............	108	——	
$C_9 H_{20}$	Butyl-amyl	132	——	
$C_{10} H_{22}$	Amyl	158	——	
$C_{12} H_{26}$	Hexyl (caproyl)	202	——	

For the purpose of examining the question of the identity or the isomerism of these hydrocarbons, I selected methyl-hexyl and hydride of heptyl, obtained from azelaic acid, comparing the properties of these bodies with ethyl-amyl, as described in my last communication.

(1) *Methyl-hexyl.*

Methyl-hexyl (methyl-caproyl) has already been prepared by Wurtz by the electrolysis of a mixture of acetate and œnanthylate of potassium, but he has obtained it in a small quantity only, and in a very impure state ‡. I adopted the same method, and am able to confirm all that Wurtz has stated. Although I employed several ounces of œnanthylate of potassium, only a very inconsiderable quantity of an aromatic oil was obtained, which, in order to isolate the hydrocarbon $C_7 H_{16}$, was first distilled with concentrated sulphuric acid, by the action of which sulphurous acid was evolved and a black charry matter separated out. The oily distillate was well washed and further purified by means of nitric acid, caustic potash, and sodium, as described in my former papers, and then the small quantity of methyl-hexyl separated by fractional distillation from hexyl, $C_{12} H_{26}$, which latter hydrocarbon is formed in by far the greatest proportion.

Methyl-hexyl boils at 89°–92° C., and has the specific gravity 0·6789 at 19° C. The analysis gave the following numbers:—

0·2002 substance gave 0·6150 carbonic acid and 0·2900 water.

	Calculated.	Found.
C_7	84	83·78
H_{16}	16	16·14
	100	99·92

* Dale, Journ. Chem. Soc. New Ser. ii. p. 258. † Ibid.

‡ Ann. de Chim. et de Phys. 3 sér. xliv. 296.

The quantity which I obtained was only sufficient for determining the boiling-point and the specific gravity, both of which nearly coincide with those of ethyl-amyl; and although I could not investigate its reactions, I believe that these also will agree with those of ethyl-amyl, so that the two hydrocarbons appear to be identical.

(2) *Hydride of Heptyl from Azelaic Acid.* By C. SCHORLEMMER and R. S. DALE, B.A.

One of us has shown that by heating a mixture of azelaic acid and caustic baryta to a dull red heat, an aromatic liquid is obtained, which chiefly consists of the hydrocarbon $C_7 H_{16}$. By oxidizing castor-oil with nitric acid on a large scale, one pound of pure azelaic acid was prepared, which yielded about one ounce of a hydrocarbon boiling between 95° and 100°. Subjected to fractional distillation, a small quantity of hydride of hexyl from the suberic acid, which still adhered to the azelaic acid, was separated, and now the liquid boiled constantly at 100°·5 C. (corrected). The sp. gr. at 20°·5 C. was found to be 0·6840.

The determination of its vapour-density gave the following results:—

Balloon + air..................	7·5660
Temperature of air	16°·5
Balloon and vapour..............	7·7830
Temperature on sealing	140°
Capacity of balloon	115·5 cub. centims.

Vapour density calculated.	Found.
3·46	3·63

This hydrocarbon is very easily attacked by chlorine, the chloride $C_7 H_{15} Cl$ being chiefly formed, together with a small quantity of higher chlorinated products.

The chloride boils at 151°–153° C., and has the specific gravity 0·8737 at 18°·5. It is a colourless liquid, smelling exactly like the chloride obtained from ethyl-amyl.

0·3045 substance gave 0·3165 chloride of silver and 0·0045 of metallic silver.

Calculated.	Found.
26·40 per cent. Cl	26·20 per cent Cl

By heating this chloride with acetic acid and acetate of potassium in sealed tubes, heptylene and acetate of heptyl are formed. This decomposition goes on much quicker than in the case of the chloride from ethyl-amyl; and the proportions of the substances formed also differ, as only a very small quantity of heptylene is produced, and the chief product consists of the acetate, whilst the chlorides from ethyl-amyl and from petroleum yield these two substances in about equal quantities.

The heptylene boils at 95°–97°, and has the specific gravity 0·7026 at 19°·5.

The faint garlic-like smell is identical with that of the heptylene described in my last paper.

0·1952 substance gave 0·6130 carbonic acid and 0·2510 water.

	Calculated.		Found.
C_7	84	85·7	85·65
H_{14}..........	14	14·3	14·28
	8	100·0	99·93

The acetate also has the same pear-like smell as the acetate from ethyl-amyl. It boils at 180°–182°, and has the specific gravity of 0·8605 at 16°.

0·2446 substance gave 0·6135 carbonic acid and 0·2540 water.

	Calculated.		Found.
C_9	108	68·35	68·40
H_{18}..........	18	11·39	11·53
O_2	32	20·26	——
	158	100·00	

From the acetate the alcohol was prepared by heating with a concentrated solution of caustic potash. Dried over caustic baryta, the alcohol boiled at 164°–167°.

The specific gravity at 19°·5=0·8286.

Its odour cannot be distinguished from that of the alcohol from ethyl-amyl.

By oxidizing it with chromic acid, first the odour of œnanthol is perceived, and then an oily acid is obtained, which by its smell, as well as the analysis of its silver-salt, was recognized as œnanthylic acid.

0·1205 of the silver-salt obtained by saturating the rectified acid distillate with carbonate of silver, gave 0·0551 of metallic silver, or 45·72 per cent., the formula $C_7 H_{13} Ag O_2$ requiring 45·57 per cent. Ag.

The annexed Table gives the boiling-points and specific gravities of the hydrocarbons $C_7 H_{16}$ of different origin, and their derivatives. From these data, as well as from the experiments detailed in this and in my former papers, it appears that we meet here with examples of absolute isomerism, viz. compounds having the same percentage composition and the same constitutional formula (A. Crum Brown), but differing from each other in their physical properties. This is not only the case with the hydrocarbons, but also, in a greater or less degree, with their derivatives.

Ethyl-amyl and hydride of heptyl from azelaic acid, as well as the corresponding chlorides, were obtained in as pure a state as possible, and in pretty large quantities; and although only small quantities of the acetate, alcohol, and olefine from the hydride were at our disposition, yet the greatest care was taken to obtain them pure, and all determination of the boiling-points and specific gravities were carried out under the same circumstances, the same thermometer always being used, so that they may be fairly compared with each other.

		Heptyl compounds derived from			
		1. Petroleum.	2. Ethyl-amyl.	3. Azelaic acid.	4. Methyl-hexyl.
$C_7 H_{16}$	Boil.-point	90°–92°(98–99°)	90°–91°	100°·5	89°–92°
	Sp. gravity	0·7148 at 15°	0·6795 at 20°	0·6840 at 20°·5	0·6789 at 19°
$C_7 H_{14}$	Boil.-point	95°–97°	93°–95°	95°–97°	
	Sp. gravity	0·7383 at 17°·5	0·7060 at 12°·5	0·7026 at 19°·5	——
$C_7 H_{15} Cl$	Boil.-point	148°–150°	146°–148°	151°–153°	
	Sp. gravity	0·8965 at 19°	0·8780 at 18°·5	0·8737 at 18°·5	——
$C_7 H_{16} O$	Boil.-point	164°–165°	163°–165°	164°–167°	
	Sp. gravity	0·8479 at 16°	0·8291 at 13°·5	0·8286 at 19°·5	——
$\left.\begin{matrix}C_7 H_{15}\\ C_2 H_3 O\end{matrix}\right\} O$	Boil.-point	179°–181°	178°–180°	180°–182°	——
	Sp. gravity	0·8865 at 190°	0·8707 at 16°·5	0·8605 at 16°	——

C. M. Warren has lately published * an investigation on the hydrocarbons contained in the American petroleum, which he isolated according to a new method of fractional condensation. He states that the petroleum contains two series of the hydrocarbons $C_n H_{2n+2}$, the isomeric pairs of which show a difference in their boiling-points of 7°–8°.

Some of the results which I have formerly obtained tend to confirm this view.

Frankland, Wurtz, Pelouze, and Cahours found 30° as the boiling-point of hydride of amyl; the hydrocarbons of the same composition, which I isolated from the light oils obtained from Cannel coal, boils constantly between 39° and 40°. The hydride of heptyl obtained from the same source boiled at 98°–99°, and the same hydrocarbon I found in American petroleum, whilst Pelouze and Cahours give 92°–94° as the boiling-point; and in my last communication I have quoted some experiments made by Mr. Wright, who found that from that part of American petroleum which boils between 95°–100° a considerable quantity of a hydrocarbon, $C_7 H_{16}$, may be obtained which boils constantly at 90°–92°. These latter hydrocarbons and their derivatives show, even after repeated rectification, higher specific gravities than the isomeric alcohol-radicals and the hydrocarbons from azelaic acid.

Thus it appears that bodies showing a purely physical isomerism are as numerous in the marsh-gas family as in the case of the terpines, $C_{10} H_{16}$.

In order to complete this investigation, I intended to study in the same manner the hydrocarbons $C_6 H_{14}$, namely hydride of hexyl from suberic acid, methyl-amyl, and, if possible, ethyl-butyl; but this intention could not be carried out, as I could not succeed in preparing methyl-amyl. This hydrocarbon appears not to be formed by any of the methods which are employed to prepare the so-called mixed alcohol-radicals. A mixture of the iodides of methyl and amyl is exceedingly slowly attacked by sodium. The boiling-point of the mixture is below the fusing-point of sodium, and the metal soon becomes coated with a hard crust of iodide of sodium. I

* Mem. American Academy, New Series, vol. ix. p. 156.

added, therefore, a sufficient quantity of pure amyl to raise the boiling point, but even the sodium in the fused state acts very slowly, a considerable quantity of gaseous products being evolved.

After the mixture had been heated for a week, large quantities of the iodides were still present, and after destroying these by strong nitric acid, the remaining hydrocarbon was found to be pure amyl.

No better results were obtained by adding anhydrous ether to the mixture. The action in the cold is exceedingly slow; heated in sealed tubes, the iodides are soon decomposed; but besides gaseous products, only amyl, and not a trace of a mixed radical, is formed.

Besides hydride of heptyl, other products are formed by the action of caustic baryta upon azelaic acid. Of those only one could be obtained in a pure state. If the aromatic liquid which is first obtained is distilled with water, hydride of heptyl chiefly distils, and a brown oily liquid remains behind, which, after cooling, solidifies to a crystalline mass containing a brown aromatic oil which may be removed from the crystals by pressing between blotting-paper. The solid substance is repeatedly recrystallized from hot diluted alcohol, in which the still adhering oil is very slightly soluble. The pure substance is thus obtained in small colourless needles, which are grouped in tufts. It is odourless and tasteless, very soluble in ether and in alcohol, insoluble in water, melts between 41° and 42°, solidifies again at 40°, and distils between 283°–285° (not corrected) without decomposition.

The following analysis shows that it has the formula $C_n H_{2n}$.

0·2480 substance gave 0·7800 carbonic acid and 0·3215 water.

	Calculated.	Found.
C_n	85·7	85·77
H_{2n}	14·3	14·40
	100·0	100·17

The quantity obtained was not sufficient to determine the vapour-density.

If this olefine is suspended in water and bromine added, not in excess, the two substances combine readily to a colourless oily liquid, the odour of which resembles bibromide of ethylene. It cannot be distilled without decomposition, and appears even to be decomposed by a diluted solution of caustic soda, as a small portion thus treated in order to remove an excess of bromine changed its odour completely. By an unfortunate accident the whole of the bromide was lost, with the exception of the portion treated with caustic soda. This was washed with water, dissolved in ether, and the ethereal solution dried with chloride of calcium. After evaporating the ether and drying the remaining small quantity of heavy yellow oil over sulphuric acid under the air-pump, only just sufficient was left to determine the bromine.

0·1500 gave 0·0736 of bromide of silver, and 0·0102 of metallic silver, corresponding to 25·8 per cent. of bromine.

From the boiling point of the olefine it appears that its molecular for-

mula is most likely $C_{16}H_{32}$; and if bromine forms the bibromide, $C_{16}H_{32}Br_2$, from which by the action of caustic soda H Br is abstracted, the compound analyzed would be $C_{16}H_{31}Br$, which formula requires 26·4 per cent. of bromine, whilst the analysis gave 25·8 per cent.; the hydrocarbon would then be an isomer of cetene.

III. "On the Laws of Connexion between the conditions of a chemical Change and its Amount." By A. Vernon Harcourt and W. Esson. Communicated by Sir B. C. Brodie, Bart., F.R.S. Received September 5, 1865.

(Abstract.)

The amount of a chemical change under any conditions which allow of its completion, depends ultimately upon the amount of that one of the substances partaking in it which is present in the smallest proportional quantity. But if the change be arrested before any one of the reagents is exhausted, its amount depends upon the conditions under which it has occurred. These conditions, in the simplest cases, are the quantity of the several reagents, their temperature, and the time during which they have been in contact. The laws of connexion between these conditions of a chemical change and its amount are the subject of an investigation upon which the authors have entered. An account of the first stage of this investigation is contained in the present paper.

Although every chemical change is undoubtedly governed by certain general laws relating to the conditions under which it occurs, the number of cases in which the investigation of these laws is possible is extremely limited. For it is requisite both that the amount of change should be readily estimated, and also that all the conditions affecting it should be susceptible of measurement and of such independent variations as must be made in order to determine the separate influence of each.

The first reaction chosen for investigation was that of permanganic acid upon oxalic acid. It is well known that when a solution of potassic permanganate is added to a solution containing an excess of oxalic acid and sulphuric acid, a change takes place which in its final result is represented by the following equation:—

$$K_2Mn_2O_8+3H_2SO_4+5H_2C_2O_4=K_2SO_4+2MnSO_4+10CO_2+8H_2O.$$

This reaction occurs at the ordinary temperature; it is thus comparatively easy to keep the temperature of the solution absolutely constant during its progress. It occupies, under a due arrangement of other conditions, a convenient interval of time, and can be started and terminated at a given moment. The reagents are readily obtained in a state of purity, and can be accurately divided and measured as liquids. Lastly, no other condition besides those named affects the result: when each of these is fixed, the amount of change observed in successive experiments is always the same. Nevertheless this reaction, as appeared in the course of its investigation, is